

The Composition and Possible Constitution of Several Sulfur Dyes

DISSERTATION

SUBMITTED TO THE BOARD OF UNIVERSITY STUDIES OF THE
JOHNS HOPKINS UNIVERSITY IN CONFORMITY WITH
THE REQUIREMENTS FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY

BY

W. NORTON JONES, JR.

Baltimore

1931

The Composition and Possible Constitution of Several Sulfur Dyes

DISSERTATION

SUBMITTED TO THE BOARD OF UNIVERSITY STUDIES OF THE
JOHNS HOPKINS UNIVERSITY IN CONFORMITY WITH
THE REQUIREMENTS FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY

BY
W. NORTON JONES, JR.

Baltimore

1931

ACKNOWLEDGMENT

The author wishes to thank Professor E. Emmet Reid, who suggested this problem and under whose direction and supervision its investigation was executed. He is grateful to Dr. Linus M. Ellis and to Dr. F. C. Wagner for advice and laboratory suggestions throughout the course of the investigation and to Drs. Lubs and Strouse of the Jackson Laboratory of E. I. du Pont de Nemours and Company for their kindness in considering on several occasions certain difficulties encountered. To Mr. N. B. Tucker also, he is grateful for the use of certain apparatus and equipment and for assistance in manipulation from time to time.

He further wishes to acknowledge certain dyes and dye intermediates furnished by E. I. du Pont de Nemours and Company.



THE COMPOSITION AND POSSIBLE CONSTITUTION OF SEVERAL SULFUR DYES

The facts that the majority of the sulfur dyes cannot be obtained in crystal form and that in most cases they form colloidal solutions have made investigation of their constitutions exceedingly difficult. However, the thiazine nature of the black and blue dyes has been established by the collection of a plethora of data from various sources.¹ The full structural formula of only one of the sulfur dyes, *Immedial Reinblau*, which forms a crystalline complex² with sodium bisulfite, has been determined and its fundamental thiazine structure thoroughly established. Since the majority of the sulfur colors are prepared from diphenylamine derivatives, dyes prepared from a few of its simplest derivatives were chosen for this investigation.

The dye known in commerce as Navy Blue RL and the three we shall designate as Bordeaux Y, Bordeaux X and Green Z were prepared by thionation under similar conditions of *p*-hydroxydiphenylamine, *p*-aminotolyl-*p*'-hydroxyphenylamine, *p*-methyl-*p*'-hydroxydiphenylamine and *p*-amino-*p*'-hydroxydiphenylamine, respectively. Investigation showed all four dyes to possess properties characteristic of the class, and efforts to determine their molecular weights by several methods were fruitless.

In preparing the dyes we endeavored to obtain samples of each dye of constant composition, it being a well-known fact that any given sulfur dye may have a widely varying sulfur content according to its conditions of fabrication. With this point in mind, great care was taken to ensure that the period and temperature of sulfuration were the same in the manufacture of each batch. Save in the instance of Green Z, the extent of sulfuration as shown by analysis was fairly constant in each case.

As a rule a sulfur dye derived from an indophenol of the type here considered contains the same nitrogen atom, or atoms, as the intermediate from which it is made; the nitrogen content of the purified product was used as the basis in calculating the empirical formulas from the analyses. The oxygen values run a bit high as is to be expected since the calculations are based on nitrogen determinations which are inclined to run low.

The results of these analyses as tabulated in Table VI show the following formulas to express the composition of the dyes: $C_{12}H_7NOS_3$ for Bor-

¹ Lange, "Die Schwefelfarbstoffe, ihre Herstellung und Verwendung," Verlag Otto Spamer, Leipzig, 1921, p. 20.

² Gnehm and co-workers, *J. prakt. Chem.*, [2] **69**, 169 (1904); *Ber.*, **37**, 2618 (1904).

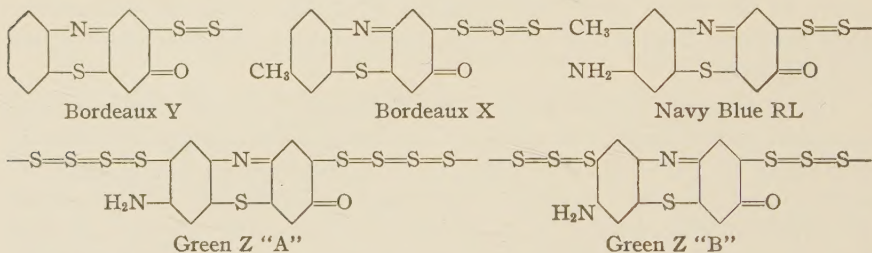
deaux Y, $C_{13}H_9NOS_4$ for Bordeaux X, $C_{13}H_{10}N_2OS_3$ for Navy Blue RL and $C_{12}H_7N_2OS_7$ and $C_{12}H_7N_2OS_9$, respectively, for the two varieties of Green Z.

The evolution as hydrogen sulfide of a portion of the sulfur contained in these compounds upon reduction with stannous chloride as shown in Table I was the most enlightening reaction encountered.

TABLE I

Dye	Bordeaux Y	Bordeaux X	N. Blue RL	Green Z "A"	Green Z "B"	(I)	(II)
No. S atoms	3	4	3	9	7	1	2
No. S atoms removed	1	2	1	6	4	0	0
No. S atoms remaining	2	2	2	3	3	1	2

From a consideration of this and certain other facts, the following structures are suggested as the units from which the various dyes investigated assemble themselves

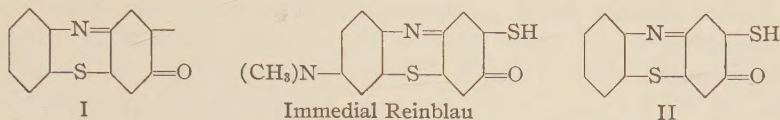


The compound containing but one atom of sulfur prepared by thionating *p*-hydroxydiphenylamine by refluxing with Na_2S_2 and water and shown to be identical with Bernthsen's³ oxo-thiodiphenylimide (I) of proved thiazine structure, was unaffected by stannous chloride and acid even when heated strongly. The very similar compound (II) described below, containing two sulfur atoms, one of which must be in the basic thiazine structure, while the other is most likely attached to one of the benzene rings in some sort of a side chain, presumably a sulfhydryl group which may react with a second such group to form a connecting disulfide, is likewise unaffected by such treatment. But the dye, Bordeaux Y, containing three sulfur atoms suffers the loss of one of them by the tin salt reduction. We have taken this to mean that the sulfur atom in the basic thiazine structure and the sulfur of the side chain which is directly attached to a carbon of one of the benzene rings are unattacked by this reducing mixture, but that the sulfur atom of the side chain other than those attached directly to a carbon are removed.

On examination of the mixture left in the reaction flask, it was seen at once that the dye, although having suffered reduction, had not been reduced to the leuco form as with caustic and with hydrosulfite. The mate-

³ Bernthsen, *Ann.*, 230, 182 (1885); *Ber.*, 17, 2860 (1884).

rial left in the flask showed properties very similar to the oxo-thiodiphenylimides.



The similarity of the two reddish-brown dyes to oxo-thiodiphenylimide (I) is a point in support of this thiazine nature. The blue dyes have long been held to be of a thiazine⁴ nature, a point that has been established by the collection of a great amount of data from various sources over a period of years. The behavior of our Navy Blue RL and Green Z supports this contention. The case of *Immedial Reinblau*, whose formula and thiazine nature are established, may be cited and the similarities pointed out. The work of other investigators on the nature of the dye from *p*-tolylamino-*p*'-hydroxyphenylamine may also be pointed out,⁵ as well as Vidal's⁶ earlier researches on the black and blue sulfur dyes.

Apparently there is but one sulfur atom in the thiazine structures of the various dyes and the sulfur in the side chains may or may not be there as polysulfides; likewise in the case of compounds containing more than enough sulfurs to satisfy the thiazine structure and the various directed positions in its rings, polysulfide chains, which may vary in length, apparently exist as proposed by Möhlaus⁷ and substantiated by the work of Schultz and Beyschlag.⁸ Whether the limit of S₈ set by Möhlaus is correct, we cannot venture to say. It is thought also that where sulfhydryl groups do exist in a unit they combine with similar groups of other units to form aggregates held together by disulfide bridges and perhaps by other means. This may account, at least in part, for the formation of indefinitely large molecules or colloidal aggregates.

It will be remembered that the two reddish dyes are prepared from compounds containing but one auxochrome group, namely, the hydroxyl group; while the intermediates of the other two colors contain both an hydroxyl and an amino group, each; one recalls also that in the case of the intermediate from which Navy Blue RL is prepared, a methyl group stands ortho to the amino group, thus blocking that position. It is generally conceded that the place of entrance of sulfur-bearing side chains into the nuclei of the dyes is in the positions ortho to auxochrome groups.⁹ Now if

⁴ Bernthsen, *Ann.*, **230**, 73 (1885); *Ber.*, **16**, 1025 and 2896 (1883).

⁵ Gnehm, *J. prakt. Chem.*, **69**, 169, 170 (1904).

⁶ Vidal, *Mon. sci.*, **17**, 427; **11**, [II] 655 (1897).

⁷ Lange, Ref. 2, p. 76; "Eigenbericht Möhlaus auf der Versamml. deutscher Naturf. u. Ärzte," Dresden, Sept., 1907.

⁸ Schultz and Beyschlag, *Ber.*, **42**, 743 and 753 (1909); *Chem.-Ztg.*, **31**, 937 (1907).

⁹ Lange, Ref. 2, p. 71; Friedländer, *Z. angew. Chem.*, **19**, 616 (1906).

these dyes be all of a thiazine nature, then the second ortho position of each of the auxochrome groups here involved is also ortho to the carbon bearing the thiazine sulfur. Such a position is rarely ever filled during dye formation except under stress of the strongest sulfuration, although the intermediate may of course bear a substituent there at the outset. Hence, in the instance of the dye from *p*-tolylamino-*p*'-hydroxyphenylamine, one should expect the extrance of but a single sulfur side chain, which indeed is apparently the case. The intermediate of Green Z possesses two auxochrome groups and no other substituents so that the entrance of two sulfur-bearing side chains would be expected during the thionation. This condition apparently obtains since three sulfurs remain after the stannous chloride reduction, whereas only two remain for the other three dyes. The two samples of Green Z also support the varying polysulfide chain idea.

Experimental

Preparation and Purification of Intermediates.—*p*-Hydroxydiphenylamine was prepared by the method of Calm.¹⁰ Attempts to employ his methods of purification were unsuccessful, so a modified method was used. The oily portion of the bomb's contents was poured into a three-liter balloon flask and the solid portion dissolved in a quantity of hot water and added to the former. The excess aniline was removed by steam distillation and the residue allowed to solidify. This was filtered off and washed with a little cold water, after which it was added to two liters of hot water containing 40 g. of solid sodium hydroxide and enough sodium hydrosulfite to prevent oxidation. This mixture was boiled until the lumps were entirely disintegrated. This mixture was filtered and the filter washed with 500 cc. of hot water containing 1 g. of sodium hydroxide and a little sodium hydrosulfite. The filtrate and washings were cooled to 20°, when 30% sulfuric acid was added with good stirring until the solution was just acid to brilliant yellow paper. This gave a heavy white precipitate, which was filtered off in an atmosphere of nitrogen in an apparatus described by Hamilton and Major.¹¹ The filter cake was dried over calcium chloride in a nitrogen-filled desiccator.

p-Methyl-*p*'-hydroxydiphenylamine was prepared in a similar manner from hydroquinone, *p*-toluidine, and calcium chloride after the method of Hatschek and Zega.¹² The reaction mixture was purified according to the foregoing method. The yield was 40%.

p-Amino-*p*'-hydroxydiphenylamine was prepared by heating for three hours at 170–180°, 73.5 g. of *p*-aminophenol, and 27 g. of *p*-phenylenediamine in a stirrer-equipped beaker resting in an oil-bath. The reaction mixture was purified by the method¹³ described above; yield, 72%.¹⁴

The fourth intermediate, *p*-aminotolyl-*p*'-hydroxyphenylamine, was furnished by E. I. du Pont de Nemours & Co.

¹⁰ Calm, *Ber.*, **16**, 2799 (1883).

¹¹ Hamilton and Major, *J. Am. Chem. Soc.*, **47**, 1131 (1925).

¹² Hatschek and Zega, *J. prakt. Chem.*, [2] **33**, 224 (1886).

¹³ Deutsche Vidal-Farbstoff-Aktiengesellschaft in Koblenz, German Patent 116,337.

¹⁴ Cf. Ullmann and Jüngel, *Ber.*, **42**, 1077 (1909), and *Ann.*, **392**, 45 (1912).

Preparation and Purification of the Dyes

Bordeaux Y.—Into a half-liter balloon flask, equipped with a short reflux condenser through which operated an electrically driven stirring device, were introduced 25 g. of *p*-hydroxydiphenylamine, 90 g. of hydrated sodium sulfide, 50 g. of flowers of sulfur and 70 cc. of distilled water. This mixture was refluxed on the oil-bath for thirty-four¹⁵ hours at 145–150° with constant stirring. When the flask had sufficiently cooled, its contents were washed into a large beaker with about a liter of distilled water, and a stream of air bubbled through the liquid for from twenty-four to forty-eight hours until the oxidized form of the dye was thrown down as a reddish solid. Care must be taken to allow during the first few hours for the excessive foaming which usually occurs.

The precipitated dye was collected on a suction filter where it was washed at some length with warm distilled water, after which it was dried in the oven at 60–80°. When dry, it was ground into a fine powder and extracted in a Soxhlet apparatus with distilled water for some twenty-four hours to remove any adsorbed sodium salts, after which it was again dried as before. It was then returned to the extractor to be washed for another twenty-four hours with carbon disulfide to remove any mechanically held sulfur. The final drying was continued for two days to ensure complete removal of all solvents employed.

A test portion of the final product upon being ignited on a clean platinum foil left in every case only an almost imperceptible trace of white soda ash.

The sulfur contents of the four batches of dye prepared from *p*-hydroxy-diphenylamine are given in the table.

TABLE II

Batch	1	2	3	4
Per cent. S	32.30	30.89	33.76	33.86

Samples of the dyes from the other intermediates were prepared in the apparatus described, under identical conditions, and were purified in the same manner. The quantities of sulfur and sodium sulfide used in each case, save that of the *p*-aminotolyl-*p'*-hydroxyphenylamine, were such that their molecular ratios to the quantity of intermediate employed were identical with the ratios in the first preparation above.

The three samples of the dye Bordeaux X were prepared by refluxing together 27 g. of *p*-methyl-*p'*-hydroxydiphenylamine, 90 g. of hydrated sodium sulfide, 50 g. of sulfur, and 70 cc. of water for thirty-four hours at 120°. ¹⁶ The following table gives their sulfur contents after purification. The ash was almost imperceptible.

TABLE III

Batch	1	2	3
Per cent. S	36.64	36.40	38.68

Although the conditions of fabrication of the two batches of Green Z were carefully controlled, the extent of sulfuration was considerably different. In both cases 28 g. of *p*-amino-*p'*-hydroxydiphenylamine, 50 g. of sulfur, 90 g. of hydrated sodium sulfide, and 70 cc. of water were refluxed together for thirty-four hours at 120°. ¹⁷

TABLE IV

Batch	1	2
Per cent. S	63.42	52.78

¹⁵ Cf. U. S. Patent 1,096,715, example 4.

¹⁶ U. S. Patent 1,098,259.

¹⁷ Meister Lucius u. Brüning, German Patent 179,884 and cf. also Deutsche Vidal-Farbstoff-Aktiengesellschaft in Koblenz, German Patents 116,337, 328,110.

The preparation of the dye known to the trade as Navy Blue RL was undertaken according to a procedure found in the patents. A mixture of 96 g. of crystalline sodium sulfide,¹⁸ 38 g. of flowers of sulfur, and 22 g. of *p*-aminotolyl-*p*'-hydroxyphenylamine was refluxed at 120° for twenty hours. The thick, blue, alkaline melt was poured into distilled water to be precipitated and purified in the usual manner. In its final form the dye is an insoluble black powder with an almost metallic luster.

TABLE V

Batch	1	2	3	4
Per cent. S	30.44	33.53	33.60	37.58

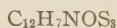
The sulfur-nitrogen ratio for different batches of the same dye was more nearly constant than the percentage of sulfur.

Determination of Empirical Formulas.—All nitrogen determinations were made by the Gunning modification of the Kjeldahl method.¹⁹ The innumerable sulfur analyses were executed by the Parr bomb method, while the carbon and hydrogen were determined by a modification of the standard combustion method.²⁰ The oxygen was, as usual, determined by difference.

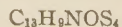
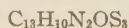
TABLE VI

ANALYSES OF DYES AND EMPIRICAL FORMULAS

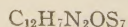
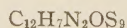
Element	Bordeaux Y—Batch 2 %	No. atoms	Bordeaux Y—Batch 3 %	No. atoms
C	51.79	12.15	50.30	10.90
H	2.52	7.04	2.68	6.90
N	4.97	1.00	5.38	1.00
S	30.89	2.72	33.76	2.74
O	9.83	1.72	8.80	1.42



	Navy Blue RL—Batch 1 %	No. atoms	Bordeaux X—Batch 3 %	No. atoms
C	47.86	12.75	45.60	12.6
H	3.22	10.28	2.65	8.7
N	8.72	2.00	4.22	1.0
S	30.44	3.04	38.68	4.0
O	9.76	1.95	8.85	1.8



	Green Z—Batch 1 %	No. atoms	Green Z—Batch 2 %	No. atoms
C	27.00	10.23	30.13	10.73
H	1.50	6.8	1.60	6.80
N	6.03	2.0	6.53	2.0
S	63.42	9.0	52.78	7.0
O	2.05	0.3	8.96	1.2



¹⁸ Leopold Cassella u. Co., G. m. b. H. in Frankfurt A./M., 1901, German Patent 199,963, example 1.

¹⁹ Leach, "Food Inspection and Analysis," 4th ed., p. 59.

²⁰ Treadwell and Hall, 1924, Vol. II, pp. 364-370.

Investigation of the Properties of the Dyes.—All four of the dyes were insoluble in water, ether, acetone, ethyl alcohol, methyl alcohol, toluene, xylene, benzene, naphthalene, concentrated hydrochloric acid, dilute sulfuric acid, concentrated acetic acid and chloroform. Their solubility and the nature of their solutions in other solvents are given in the table.

TABLE VII

Solvent	Character of solution			
	Bordeaux Y	Bordeaux X	Green Z	Navy Blue RL
H ₂ SO ₄ concd.	Deep blue	Deep purple	Slightly sol.	Blue
Aq. Na ₂ S	Clear brown	Clear brown	Clear green	Clear purple
Pyridine, hot	Deep cherry-red	Deep cherry-red	Insoluble	Deep blue
Pyridine, cold	Slightly soluble	Slightly soluble	Insoluble	Slightly soluble
Aniline, hot	Deep cherry-red	Deep cherry-red	Insoluble	Very slightly sol.
Aniline, cold	Slightly soluble	Very slightly sol.	Insoluble	Insoluble

For the most part, chemical treatment of the four dyes chosen yielded scarcely any results. As shown by the preceding table, all four dyes were soluble in strong aqueous sodium sulfide solution and likewise in caustic solution containing sodium hydrosulfite. From these solutions the addition of dilute hydrochloric acid precipitated the leuco forms of the dyes which began immediately to reoxidize to the dark insoluble dyes.

Samples of the various dyes were refluxed for long periods of time with acetic anhydride, acetyl chloride, monochloroacetic acid, benzyl chloride, benzoyl chloride and *p*-nitrobenzylbromide, respectively, with little or no results. Treatment of Bordeaux Y and Bordeaux X with benzoyl chloride and benzyl chloride, respectively, yielded small amounts of tarry substances which defied identification, while the other two dyes were unaffected.

Attempts to prepare crystalline bisulfite complexes after the method of Gnehm²¹ and his co-workers in the case of *Immedial Reinblau* were fruitless.

Oxidation of the dyes by concentrated nitric acid and fusion with sodium hydroxide produced in every case such a complete disruption of the molecule that little concerning its structure could be deduced from the products thereof.

Alkylation undertaken by treating the reduced caustic solutions of the dyes with redistilled dimethyl sulfate gave precipitates ranging in color, according to the dye involved, from bright yellow to brown, which were immediately oxidized, even in an inert atmosphere, to dark insoluble substances.

Solutions of the dyes in aqueous sodium sulfide upon examination with the ultramicroscope were found to be colloidal in nature, and x-ray diffraction photographs of the dye from *p*-hydroxydiphenylamine showed only a single broad band about one centimeter from the primary beam, a diagram which is characteristic of non-crystalline substances. Solutions of the dyes in pyridine and aniline showed no raising of the boiling point and only a

²¹ Gnehm and co-workers, *J. prakt. Chem.*, [2] **69**, 169 (1904); *Ber.*, **37**, 2618 (1904).

slight depression of the freezing point, so no estimation of the molecular weights could be made. In fact, a slight depression of the boiling point was observed probably due to the presence of traces of moisture.

Other Compounds Prepared by the Sulfuration of *p*-Hydroxydiphenylamine.—Treatment similar to that of *p*-hydroxydiphenylamine in the preparation of Bordeaux Y was accorded another portion of the intermediate with a polysulfide mixture corresponding to Na_2S_2 and the product was purified by the method cited above. Analysis showed the presence of but one sulfur atom, and it was shown to be identical with the oxo-thiodiphenylimide prepared by the method of Bernthsen.²²

Yet another portion of the *p*-hydroxydiphenylamine was treated in the usual manner with a polysulfide mixture corresponding to Na_2S_3 . On purification of the product by the method described above, analysis showed the presence of two sulfur atoms for each nitrogen.

Both of the foregoing compounds in caustic solution suffered reduction by treatment with sodium hydrosulfite, both dissolved in concentrated sulfuric acid with the deep blue color characteristic of the dye, and both are likewise reprecipitated as the reddish solid by addition of water to the strong acid solution. This latter compound is held to be that represented by formula (II) above, or a compound composed of aggregates of these units, which seems more likely.

Reduction of the Dyes with Stannous Chloride.—Samples of one- or two-tenths of a gram of the respective dyes and sulfur compounds were introduced into a two-necked half-liter balloon flask connected to a reflux condenser fitted with a delivery tube fashioned from a 25-cc. pipet. To this was added a mixture of 47 cc. of glacial acetic acid, 2 cc. of concentrated hydrochloric acid and 1 cc. of sirupy phosphoric acid and 10 g. of stannous chloride after the method of Sampey.²³ The apparatus was made air-tight and the outlet of the delivery tube was placed beneath the surface of a portion of the reagent prepared from 10 g. of zinc sulfate, 450 cc. of concd. ammonia and 500 g. of distilled water. The mixture in the flask was heated with a small flame for some sixteen hours while a stream of nitrogen, purified by passage through a wash bottle containing a caustic solution of pyrogallol and thence through a drying tower, was forced through the apparatus.

As the heating continued, a stream of hydrogen sulfide was evolved to be swept out by the nitrogen and precipitated as zinc sulfide which was collected when the reaction was completed and the sulfur determined by the usual iodimetric method. That there was some loss of hydrogen sulfide due to the makeshift nature of the apparatus there can be no doubt.

The amount and percentage of sulfur evolved from the several dyes are given in the table.

²² Bernthsen, *Ann.*, **230**, 182 (1885); *Ber.*, **17**, 2860 (1884).

²³ J. R. Sampey, Jr., "A Development in Project 28," *Am. Pet. Inst.*

TABLE VIII

Dye Sample	Bordeaux Y		Bordeaux X		Green Z "A"	
	1	2	1	2	1	2
Dye	0.1767	0.2069	0.1002	0.1431	0.1234	0.1198
S evolved	0.01849	0.02147	0.019397	0.023717	0.050498	0.04985
% S evolved	10.47	10.38	19.36	16.57	40.92	41.61
No. S evolved	0.85	0.84	2.001	1.71	5.8	5.9
Dye Sample	Green Z "B"		Navy Blue RL			
	1	2	1	2		
Dye	0.0977	0.1381	0.1041	0.1025		
S evolved	0.02955	0.03832	0.009602	0.009256		
% S evolved	30.25	27.75	9.23	9.03		
No. S evolved	4.03	3.70	0.925	0.907		

Summary

1. Dyes were prepared by the thionation of *p*-hydroxydiphenylamine, *p*-methyl-*p'*-hydroxydiphenylamine, *p*-amino-*p'*-hydroxydiphenylamine, and *p*-aminotolyl-*p'*-hydroxyphenylamine. Certain sulfurated derivatives of *p*-hydroxydiphenylamine were also prepared.

2. These dyes were purified and analyzed, and their properties and reactions were investigated.

3. The evolution of a part of the sulfur of these compounds as hydrogen sulfide upon their being heated with stannous chloride and strong acid was the most enlightening reaction encountered.

4. The respective units of which the aggregates of all four dyes are composed are apparently of a thiazine nature and bear polysulfide chains of varying sulfur content attached to the rings composing the nucleus. The longest polysulfide chain encountered contained four sulfur atoms.

5. Constitutional formulas for the four units involved are suggested.

BIOGRAPHY

William Norton Jones, Jr., was born November 16, 1908 at Augusta, Arkansas. He was graduated from the Little Rock High School in June, 1924, and in the autumn of that same year entered Hendrix College, Conway, Arkansas. In June, 1928, he was granted the degree of Bachelor of Arts, *magna cum laude*, by that institution.

He entered the Johns Hopkins University in the autumn of 1928 where he has since been engaged in the study of chemistry with organic chemistry as his major subject. In June, 1930, he was granted the degree of Master of Arts. For the academic year 1930-31 he held an assistantship in organic chemistry.

